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(71)Applicant: TOAGOSEI CO LTD

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(72)Inventor: NIWA MAKOTO

OTA HIROYUKI

(54) ACTIVE ENERGY RAY CURING TYPE COMPOSITION FOR COATING PLASTICS

(57)Abstract:

PURPOSE: To obtain the subject composition, comprising a specific compound containing the oxetane ring and a cationic photopolymerization initiator, having a high curing rate, excellent in adhesion, scuff resistance and surface smoothness of a film and useful for hard coating of a plastics.

3

CONSTITUTION: This composition comprises (A) a compound having 1-4 oxetane rings {e.g. a compound of formula I [R1 is H, a 1-6C (fluoro)alkyl, allyl, etc.; R2 is a 1-6C alkyl, a 2-6C alkenyl, phenyl, etc.] or a compound of formula II [R3 is a (branched) alkylene, a (branched) poly(alkyleneoxy), a bivalent unsaturated hydrocarbon group, etc.]} and (B) a cationic photopolymerization initiator (e.g. a diaryliodonium salt or a triarylsulfonium salt) and as necessary further (C) a compound containing

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salt) and, as necessary, further (C) a compound containing epoxy group, (D) a compound containing vinyl ether group or (E) a compound containing (meth)acryloyl group and a photopolymerization free radical initiator.

LEGAL STATUS



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- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[Industrial Application] This invention relates to the activity energy-line hardening setup-of-tooling product for plastic linings which consists of a compound which has an oxetane ring, and the object for prizes is carried out in the field which manufactures and uses plastics, especially the field of the rebound ace court of plastics. In addition, in this specification, an acryloyl radical or a methacryloyl radical is expressed as an acryloyl (meta) radical.

[10002]

[Description of the Prior Art] Plastic material is used for various applications as alternate material, such as a metallic material, taking advantage of the features, such as that tough nature and workability, however in order that that front face may tend to get damaged softly in many cases and plastic material may solve this problem, many methods of improving the degree of hardness and abrasion-proof nature on the front face of plastic material are proposed conventionally. As the example of representation, there is covering on the front face of plastic material by the activity energy-line hardening setup-of-tooling product hardened with activity energy lines, such as ultraviolet rays or an electron ray. ** with long ** pot life with quick ** cure rate as features of this approach which can acquire a broad property by selection of the oligomer as a ** hardening component -- it is essentially a non-solvent system -- etc. -it is mentioned. However, as for most activity energy-line hardening setup-of-tooling products for covering of conventional plastic material, although the polyfunctional acrylate or unsaturated polyester hardened according to an activity energy-line initiation radical polymerization was used, generally, film thickness suited the inclination of these which is large as for the effect of the polymerization inhibition by oxygen, and spoils the hardenability of a constituent, the abrasion-proof nature of the paint film obtained, surface smooth nature, etc. for the application of several micrometer order and a thin plastic lining at the time of hardening.

[0003] As activity energy-line hardening techniques other than an activity energy-line initiation radical polymerization, the activity energy-line initiation cationic polymerization technique is put in practical use. Since especially activity energy-line initiation cationic polymerization is not checked by oxygen, there is no limit that it must carry out under an inert atmosphere, and it has the advantage that a prompt and perfect polymerization can be performed in air. The activity energy-line initiation cationic polymerization technique was concentrated on the polymerization of two kinds of monomers called an epoxy resin and vinyl ether till today. Especially a photoresist epoxy resin is excellent in an adhesive property, and the paint film has thermal resistance and good chemical resistance. However, in the conventional photoresist epoxy resin, since it had the defect in which a photopolymerization rate is comparatively slow, it was not able to be used in the application asked for prompt photo-curing. Moreover, toxicity including mutation is pointed out and, as for the photoresist epoxy resin of low molecular weight, the danger is regarded as questionable. On the other hand, it is volatile, or there are many strong things of an odor, the contraction at the time of hardening is accepted as compared with photoresist epoxy, and photoresist vinyl ether has many which have not enough adhesion.

[0004]

[Problem(s) to be Solved by the Invention] By excelling in the hardenability which solves these problems, this invention persons inquired wholeheartedly in order to find out the activity energy-line hardening setup-of-tooling product for the plastic lining the paint film excels [plastic lining] in adhesion, abrasion-proof nature, and surface smooth nature further. [0005]

[Means for Solving the Problem] this invention persons completed header this invention for the ability of the constituent which consists of cyclic ether which has specific structure by various examination to solve the above-mentioned technical problem as an activity energy-line hardening setup-of-tooling product for plastic linings. Namely, the activity energy-line hardening setup-of-tooling product for plastic linings which consists of a compound with which the 1st invention of this invention has 1-4 oxetane rings, and an optical cationic initiator, The activity energy-line hardening setup-of-tooling product for plastic linings of the 1st invention which contains further the compound with which the 2nd invention has an epoxy group, The activity energy-line hardening setup-of-tooling product for plastic linings of the 1st invention which contains further the compound with which the 3rd invention has a vinyl ether radical, or the 2nd invention, The 4th invention is the activity energy-line hardening setup-of-tooling product for plastic linings of the 1st invention which contains further the compound and the optical radical polymerization initiator which have an acryloyl (meta) radical, the 2nd invention, or the 3rd invention. Hereafter, this invention is explained to a detail.

[0006] O The compound which has the oxetane ring used by compound this invention which has 1-4 oxetane rings has 1-4 oxetane rings. When the compound which has five or more oxetane rings is used, flexibility is lost by the hardening film of a constituent and a cracking crack may be caused by bending. Various things can be used for it if the compound which has the oxetane ring used by this invention is a compound which has 1-4 oxetane rings. As a compound which has one oxetane ring, the compound shown by the following general formula (1) is mentioned.

[Formula 1]
$$\mathbb{R}^{1}$$
 \mathbb{R}^{2} (1)

[0008] It sets at a ceremony (1) and is R1. They are the alkyl group of 1-6 carbon numbers, such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, or butyl, the fluoro alkyl group of 1-6 carbon numbers, an allyl group, an aryl group, a furil radical, or a thienyl group. R2 The alkyl group of 1-6 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, 1-propenyl radical, 2-propenyl radical, a 2-methyl-1-propenyl radical, The alkenyl radical of 2-6 carbon numbers, such as a 2-methyl-2-propenyl radical, 1-butenyl group, 2-butenyl group, or 3-butenyl group, The radical which has rings, such as a phenyl group, benzyl, fluoro benzyl, a methoxybenzyl radical, or a phenoxy ethyl group, The alkyl carbonyl group of 2-6 carbon numbers, such as an ethyl carbonyl group, a propylcarbonyl radical, or a butyl carbonyl group, The alkoxy carbonyl group of 2-6 carbon numbers, such as an ethoxycarbonyl radical, Or it is N-alkyl carbamoyl group of 2-6 carbon numbers, such as an ethyl carbamoyl group, a propyl carbamoyl group, a butylcarbamoyl radical, or a pentyl carbamoyl group, etc.

[0009] Next, as a compound which has two oxetane rings, the compound shown by the following general formula (2) is listed.

[0010]
[Formula 2]
$$R^1$$
 O
 R^3
 O
 R^1
(2)

[0011] It sets at a ceremony (2) and is R1. It is the same radical as the thing in said general formula (1). R3 For example, they are the alkylene group containing lines, such as lines, such as lines, such as ethylene, a propylene radical, or a butylene radical, or a branching-like alkylene group, a poly (ethyleneoxy) group, or the Pori (propyleneoxy) radical, or a branching-like Pori (alkyleneoxy) radical, a pro PENIREN radical, a methyl pro PENIREN radical, or a butenylene radical, or a branching-like unsaturated hydrocarbon radical, a carbonyl group, and a carbonyl group, an alkylene group containing a carboxyl group, or an alkylene group containing a carbamoyl group. Moreover, R3 It is also the polyad chosen from the radical shown by the following type (3), (4), and (5).

[Formula 3]
$$-CH_2$$
 $-CH_2$ (3)

[0013] It sets at a ceremony (3) and is R4. The alkyl group of 1-4 carbon numbers, such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, or butyl, They are halogen atoms, such as an alkoxy group of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, or a butoxy radical, a chlorine atom, or a bromine atom, a nitro group, a cyano group, a sulfhydryl group, a low-grade alkyl carboxyl group, a carboxyl group, or a carbamoyl group. [0014]

$$\begin{array}{c|c}
 & \text{[Formula 4]} \\
 & \text{CH}_2 \\
 & \text{R}_2
\end{array}$$
(4)

[0015] a formula (4) -- setting -- R5 An oxygen atom, a sulfur atom, a methylene group, NH, SO and SO2, and C (CF3)2 Or C(CH3) 2 it is .
[0016]

[Formula 5]

$$\begin{array}{cccc}
R^{6} & R^{7} & R^{6} \\
 & | & | & | & | \\
 & (CH_{2})_{\overline{3}} & Si - O - (Si - O)_{\overline{n}} & Si - (CH_{2})_{\overline{3}} \\
 & | & | & | & | \\
 & R^{6} & R^{7} & R^{6} \\
\end{array}$$
(5)

[0017] It sets at a ceremony (5) and is R6. They are the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, or an aryl group. n is the integer of 0-2000. R7 They are the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, or an aryl group. R7 It is also the radical chosen from the radical shown by the following formula (6).

[0019] It sets at a ceremony (6) and is R8. They are the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, and butyl, or an aryl group. m is the integer of 0-100. As an example of a compound of having two oxetane rings, the compound shown by the following formula (7) and (8) is mentioned.

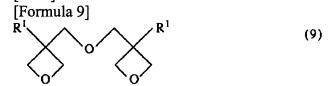
[0020]

[Formula 7]
$$O$$
 C O O O O O O O O O

[0021] It sets at a ceremony (2) and the compound shown by the formula (7) is R1. An ethyl group and R3 It is the compound which is a carboxyl group.

[Formula 8]
$$\begin{array}{c|c}
CH_3 & CH_3 \\
 & | \\
Si - O \\
 & | \\
CH_3 &$$

[0023] It sets to a general formula (2) and the compound shown by the formula (8) is R1. An ethyl group and R3 are R6 at a formula (5). And R7 They are a methyl group and the compound whose n is 1. [0024] In the compound which has two oxetane rings, there is a compound shown by the following general formula (9) as desirable examples other than the above-mentioned compound. It sets at a ceremony (9) and is R1. It is the same radical as the thing in said general formula (1). [0025]



[0026] As a compound which has 3-4 oxetane rings, the compound shown by the following general formula (10) is mentioned.

[0027]

[Formula 10]
$$\begin{bmatrix} R^1 \\ O \end{bmatrix}_j$$
(10)

[0028] It sets at a ceremony (10) and is R1. It is the same radical as the thing in said general formula (1). R9 For example, the following type (11) Branching-like polysiloxy radicals, such as a radical shown by a branching-like Pori (alkyleneoxy) radical or the following formulas (15), such as a branching-like alkylene group of the carbon numbers 1-12, such as a radical shown by - (13), and a radical shown by the following formula (14), etc. are mentioned. j is 3 or 4.

[Formula 11]

$$CH_2-$$

 $R^{10}-C-CH_2-$
 CH_2-
(11)

[0030] In [type (11), R10 is low-grade alkyl groups, such as a methyl group, an ethyl group, or a propyl group.]
[0031]

[Formula 12]

$$CH_2-$$

 $-CH_2-C-CH_2-$
 CH_2-
(12)

[0032]
[Formula 13]

$$- \text{CH}_2 - \text{CH}_2 -$$

[0033]

[Formula 14]

$$\begin{array}{c} \text{CH}_2 \longrightarrow \text{COCH}_2\text{CH}_2 \xrightarrow{1} \\ \longrightarrow \text{CH}_2\text{CH}_2\text{O} \xrightarrow{1} \text{CH}_2 \longrightarrow \text{CH}_2\text{CH}_3 \\ \longrightarrow \text{CH}_2 \longrightarrow \text{COCH}_2\text{CH}_2 \xrightarrow{1} \end{array}$$

[0034] In [type (14), 1 is the integer of 1-10.] [0035]

[Formula 15]

[0036] As an example of a compound of having 3-4 oxetane rings, the compound shown by the following formula (16) is mentioned.
[0037]

[Formula 16]

$$\begin{pmatrix}
\text{CH}_3 \\
\text{Si} - \text{O} \\
\text{CH}_3
\end{pmatrix} \text{Si}$$
(16)

[0038] Furthermore, as an example of the compound which has 1-4 oxetane rings except having described above, there is a compound shown by the following formula (17). [0039]

[0039]
[Formula 17]
$$R^{11} = O = \begin{bmatrix} R^8 \\ S_1 \\ S_1 \\ C_1 \end{bmatrix} = O = \begin{bmatrix} R^{11} \\ C_1 \\ C_2 \end{bmatrix}_3$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

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$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

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$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_1 \\ C_2 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_2 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O = \begin{bmatrix} R^1 \\ C_3 \\ C_3 \end{bmatrix}_{1}$$

$$O$$

[0040] It sets at a ceremony (17) and is R8. It is the same radical as the thing in a formula (6). R11 is the alkyl group or trialkylsilyl groups of carbon numbers 1-4, such as a methyl group, an ethyl group, a propyl group, or butyl, and r is 1-4.

[0041] There is a compound shown below as a desirable example of the oxetane compound used by this

invention.

[0042]

[Formula 18]

[Formula 19]

[0044]

[Formula 20]

[0045]

[Formula 21]

$$CH_3 CH_2 C + CH_2 - O$$

$$(21)$$

[0046] Moreover, the compound which has 1-4 oxetane rings which have the with a molecular weight of about 1000 to 5000 amount of macromolecules besides these is also mentioned. The following compounds are mentioned as these examples. [0047]

[Formula 22]

[0048] Here, p is 20-200.

[0049]

[Formula 23]

[0050] Here, q is 15-100.

[0051]

[Formula 24]

[0052] Here, s is 20-200.

[0053] O Various things can be used as an optical cationic initiator used with the constituent of optical cationic initiator this invention. A diaryl iodonium salt and a triarylsulfonium salt are mentioned as a thing desirable as these initiators. A typical optical cationic initiator is shown below. [0054]

[Formula 25]
$$R^{12} \longrightarrow I^{+} \longrightarrow$$

$$MX_{k+1}^{-}$$
(25)

[Formula 26]

$$\begin{array}{c}
MX_{\overline{k}+1} \\
S^{+} \\
\end{array}$$

$$\begin{array}{c}
R^{12} \\
\end{array}$$
(26)

[0056]

[Formula 27]

$$\begin{array}{c|c}
& MX_{k+1} \\
& S^{+} \\
& S \\
\end{array}$$
(27)

[0057]

[Formula 28]

$$\begin{bmatrix} R^{13} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

[0058] R12 is a hydrogen atom, the alkyl group of carbon numbers 1-18, or the alkoxy group of carbon numbers 1-18 among a formula, and R13 is a hydrogen atom, a hydroxyalkyl radical, and a hydroxy alkoxy group, and is a hydroxy ethoxy radical preferably. M -- a metal -- desirable -- antimony -- it is --X -- a halogen -- it is a fluorine preferably, and k is a metaled valence, for example, in the case of antimony, it is 5. As for an optical cationic initiator, it is desirable to contain at 0.1 - 20% of the weight of a rate to those total quantities, when making the compound which has the compound and/or vinyl ether radical which have an epoxy group further in this contain as opposed to the compound which has an oxetane ring, and it is 0.1 - 10 % of the weight more preferably. When not filling to 0.1% of the

weight, hardenability becomes less enough, when exceeding another side and 20 % of the weight, light transmission nature becomes poor, uniform hardening may not be able to be performed or the smooth nature on the front face of a paint film may be lost.

[0059] In addition, in each above-mentioned combination type showing the compound or the optical cationic initiator which has 1-4 oxetane rings, even if each radical expressed with the same notation which exists in 1 molecule is mutually the same, it may differ.

[0060] O Other components can be blended with the constituent of other compound this inventions if needed besides the above-mentioned indispensable component. The 2nd invention of this invention is an activity energy-line hardening setup-of-tooling product for PURASUTCHIKKU covering containing the compound which has an epoxy group further in the constituent of the 1st invention. In this case, the cure rate of a constituent is further improvable by making an epoxy compound contain in a constituent. Various things can be used as a compound which has an epoxy group. For example, as an epoxy compound which has one epoxy group, there are phenyl glycidyl ether, butyl glycidyl ether, etc., and hexanediol diglycidyl ether, tetraethylene glycol diglycidyl ether, trimethylolpropane triglycidyl ether, bisphenol A diglycidyl ether, a novolak mold epoxy compound, etc. are mentioned as an epoxy compound which has two or more epoxy groups. It is desirable especially to use an alicyclic epoxy compound by this invention, for example, the compound shown below is mentioned.

[0062]

[0063]

[0064] In this case, as the blending ratio of coal of a compound which has an epoxy group, 5 - 95 weight section is desirable to the total quantity 100 weight section of the compound which has the 1-4 above-mentioned oxetane rings, and the compound which has an epoxy group.

[0065] The 3rd invention of this invention is an activity energy-line hardening setup-of-tooling product for PURASUTCHIKKU covering containing the compound which has a vinyl ether radical further in the constituent of the 1st invention. In this case, the cure rate of a constituent is further improvable by making the compound which has a vinyl ether radical contain in a constituent. Various things can be used as a compound which has a vinyl ether radical. For example, as a compound which has one vinyl ether radical, hydroxyethyl vinyl ether, hydroxy butyl vinyl ether, dodecyl vinyl ether, propenyl ether propylene carbonate, cyclohexyl vinyl ether, etc. are mentioned. As a compound which has two or more vinyl ether radicals, the cyclohexane dimethanol divinyl ether, triethylene glycol divinyl ether, the novolak mold divinyl ether, etc. are mentioned. In this case, as the blending ratio of coal of a compound which has a vinyl ether radical, 5 - 95 weight section is desirable to the total quantity 100 weight section of the compound which has the 1-4 above-mentioned oxetane rings, and the compound which has a vinyl ether radical.

[0066] The 4th invention of this invention is an activity energy-line hardening setup-of-tooling product for PURASUTCHIKKU covering containing the compound and the optical radical polymerization initiator which have an acryloyl radical further (meta) in the constituent of the 1st invention. In this case, reforming of adjustment of constituent viscosity and the paint film degree of hardness of a constituent can be performed by making the compound which has an acryloyl (meta) radical contain in a constituent. (Meta) Various things can be used as a compound which has an acryloyl radical. For example, as a compound which has one acryloyl (meta) radical, the acrylate (meta) of the alkylene oxide addition product of these alcohol etc. is mentioned to the acrylate (meta) of a phenol, nonyl phenol, and 2-ethylhexanol, and a list. (Meta) As a compound which has two acryloyl radicals, the di(meth)acrylate of the alkylene oxide addition product of these alcohol etc. is mentioned to the di(meth)acrylate of bisphenol A, isocyanuric acid, ethylene glycol, and propylene glycol, and a list. (Meta) As a compound which has three acryloyl radicals, the Tori (meta) acrylate of the alkylene oxide addition product of these alcohol etc. is in pentaerythritol, trimethylol propane and the Tori (meta) acrylate of isocyanuric acid, and a list, and the Pori (meta) acrylate of pentaerythritol and dipentaerythritol etc. is mentioned as a compound which has four or more acryloyl (meta) radicals. Moreover, acrylic monomer oligomer with conventionally well-known the urethane acrylate which uses a urethane bond as a principal chain, the polyester acrylate which uses an ester bond as a principal chain, the epoxy (meta) acrylate which added the acrylic acid to the epoxy compound etc. is mentioned. In this case, as the blending ratio of coal of a compound which has an acryloyl (meta) radical, 5 - 95 weight section is desirable to the total quantity 100 weight section of the compound which has the 1-4 above-mentioned oxetane rings, and the compound which has an acryloyl (meta) radical. An optical radical polymerization initiator is blended with a constituent in the 4th invention of this invention. Various things can be used as an optical radical polymerization initiator. As a desirable thing A benzophenone and its derivative, benzoin alkyl ether, 2methyl [4-(methylthio) phenyl]-2-morpholino-1-propanone, Benzyl dimethyl ketal, 1-hydroxy cyclohexyl phenyl ketone, 2-hydroxy - 2-methyl-1-phenyl propane-1-ON, alkyl phenylglyoxylate, a diethoxy acetophenone and 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)-1-butane -- non, acyl phosphine oxide etc. is mentioned to a list. As for the content of these optical radical polymerization initiators, it is desirable that it is 0.01 - 20 % of the weight to the compound which has an acryloyl (meta) radical.

[0067] Moreover, in this invention, one sort chosen from the compound which has the epoxy group described above to the constituent of the 1st invention, and the compound which has an acryloyl (meta) radical in the compound list which has a vinyl ether radical, or two sorts or more can also be blended. In this case, it is desirable that it is 5 - 95 weight section about the compound which has 1-4 oxetane rings on the basis of the total quantity 100 weight section of a compound which has the compound which has the 1-4 above-mentioned oxetane rings which are hardenability components as these blending ratio of coal, the compound which has an epoxy group, the compound which has a vinyl ether radical, and (meta) an acryloyl radical.

[0068] Inerts like an inorganic bulking agent, a color, a pigment, a viscosity modifier, a processing agent, an organic solvent, and an ultraviolet-rays cutoff agent can be blended with the constituent of this invention in the amount to the 100 weight sections per hardenability component 100 weight section. [0069] The photosensitizer other than an optical cationic initiator or/and an optical radical polymerization initiator can be added to the constituent of this invention, and the wavelength of UV field can also be adjusted to it. as the typical sensitizer which can be used in this invention -- Crivello -- what [J.V.Crivello, Adv.in Polymer Sci., 62, and 1 (1984)] are indicating is mentioned, and, specifically, there are a pyrene, perylene, an acridine orange, a thioxan ton, 2-chloro thioxan ton, a benzoflavin, etc. [0070] O The constituent of operation this invention can be liquefied, it can apply to covering of various plastic material, a polycarbonate, polymethylmethacrylate, polyethylene terephthalate, vinyl chloride resin, ABS plastics, etc. can be mentioned as plastic material, for example, and the shape of tabular or fame has as these. Although what is necessary is just to also choose suitably the thickness on the plastic material front face of the constituent of this invention according to the application to be used, as desirable thickness, it is 1-50 micrometers, and is 3-20 micrometers more preferably. After using a

coating machine and applying the constituent of this invention on a plastic material front face by the approach of dipping, a flow coat, a spray, a bar coat, a gravure coat, a roll coat, a blade coat, or the Ayr knife coat that what is necessary is not to limit especially the operation of the constituent of this invention, either, but just to carry out according to the approach learned conventionally, there is the approach of irradiating an activity energy line and hardening it etc. As an activity energy line, ultraviolet rays, an X-ray, an electron ray, etc. are mentioned. Various things can be used as the light source which can be used when making it harden by ultraviolet rays, for example, pressurization or a high-pressure mercury-vapor lamp, a metal halide lamp, a xenon lamp, an electrodeless discharge lamp, or a carbon arc lamp is mentioned. When making it harden with an electron ray, what various irradiation equipment can be used, for example, a cock loft WARUTOSHIN mold, a BANDE graph mold, or a resonance transformer mold is mentioned, and has 50-1000eV energy as an electron ray is desirable, and is 100-300eV more preferably. Since cheap equipment can be used in this invention, it is desirable to use ultraviolet rays for hardening of a constituent. After carrying out coating of the constituent of this invention to plastic material, shaping, printing, or an imprint is also processible if needed. In fabricating, after heating the plastic material which has the constituent paint film of this invention to suitable temperature, the approach of performing shaping containing the plastic material performed using approaches, such as a vacuum forming, vaccum pressure sky shaping, pressure forming, or mat molding, the approach of fabricating only a coat like [in the case of carrying out embossing shaping of the uneven configurations, such as an interference fringe, on the constituent paint film of this invention like the duplicate of CD or a record], etc. are mentioned. When printing, the usual printing machine is used on a paint film, and it prints by the usual approach. When imprinting, the constituent of this invention is applied to a base material like a polyethylene terephthalate film, and if required, above-mentioned printing, above-mentioned embossing shaping, etc. will be performed, and it will imprint to other base materials after applying a glue line.

[0071] [Examp

[Example] An example and the example of a comparison are given to below, and this invention is explained more concretely. In addition, the section in each following example is weight criteria. [0072] Stirring mixing of the following compound (33) (henceforth Component G) 4 section was carried out as the following compound (32) (henceforth Component A) 100 section which has the manufacture oxetane ring of an example 1- constituent and which has the two following oxetane rings as a compound, and an optical cationic initiator, and the activity energy-line hardening setup-of-tooling product for plastic linings was manufactured. [0073]

[0075] - coating of the evaluation profit **** constituent was carried out by the thickness of 10 micrometers on the transparent polycarbonate plate, this is repeated on condition that conveyor speed 10 m/min in under the high-pressure mercury lamp of 80W [cm]/and a condensing mold to 10cm location, the bottom of a mercury lamp was passed, and it was made to harden The following evaluations were performed about the constituent and hardening film which were obtained. The result is

shown in the following table 2.

[0076] O The count of pass (count of passage) until adhesiveness disappears from a front face on the hardenability above-mentioned hardening conditions estimated.

[0077] O an adhesion profit **** paint film -- JISK Adhesion was evaluated according to the X cut tape method of 5400. In addition, O in Table 2, **, and x show following semantics.

O: JISK The evaluation mark of 5400 are 10 or 8**:JISK. The evaluation mark of 5400 are 6 or 4x:JISK. The evaluation mark of 5400 are 2 or 0 [0078]. O about the transparency profit **** paint film, it became cloudy according to JIS7105, and ** was measured. (100 Td: Becoming cloudy **=Td/Ttx scattered-light line permeability, Tt: total light transmission)

In addition, O in Table 2, **, and x show following semantics.

O [0079] exceeding less than [:1%] **:1-5%x:5% O -proof -- the abrasion of the paint film front face was carried out by abrasion nature steel wool #0000, it got damaged and the degree was observed by viewing. In addition, O in Table 2, **, and x show following semantics.

O: -- **: to which a blemish sees and is hardly stopped -- x: to which a blemish sees and is stopped slightly -- many blemishes -- **** and ******** [0080] O the surface Taira slippage profit **** paint film front face was observed by viewing. In addition, O in Table 2, **, and x show following semantics. O: fitness **: -- x: with slight turbulence -- [0081] with turbulence of many The constituent was manufactured like the example 1 except having used the component of the presentation shown in two to example 6 table 1. The activity energy-line hardening setup-of-tooling product for plastic linings was manufactured like the example 1 using the obtained constituent. About the obtained hardening film, it evaluated like the example 1. Those results are shown in Table 2.

[0082] The constituent was manufactured like the example 1 except having used the component of the presentation shown in one to example of comparison 3 table 1. The activity energy-line hardening setup-of-tooling product for plastic linings was manufactured like the example 1 using the obtained constituent. About the obtained hardening film, it evaluated like the example 1. Those results are shown in Table 2.

[0083]

[Table 1]

	A	В	С	D	Е	F	G	Н
実施例1	100						4	
実施例2	50	50					4	
実施例3			25		75		4	
実施例4	75					25	3	1
実施例 5	50				25	25	3	1
実施例6	75			25			4	
比較例1					100		4	
比較例2				75	25		4	
比較例3					75	25	3	1

[0084] In Table 1, several show the section each. Moreover, in Table 1, component B-H shows the following compounds.

[0085] - Component B [the bottom-type (34) compound which has three oxetane rings] [0086]

[Formula 34]
$$CH_3CH_2C + CH_2-O \longrightarrow 0$$

$$(34)$$

[0087] - Component C [the bottom-type (35) compound which has one oxetane ring] [0088]

[Formula 35]

[0089] - Component D [the bottom-type (36) compound which has two epoxy groups] [0090]

[Formula 36]

[0091] - Component E [the bottom-type (37) compound which has two vinyl ether radicals]

[0092]
[Formula 37]

$$CH_2 = CH - O + (CH_2CH_2O) + CH_2CH_2O +$$

[0093] - Component F [the bottom-type (38) compound which has two acryloyl radicals] [0094]

$$CH_2 = CHCO - (CH_2)_6 OCCH = CH_2$$

$$O O$$
(38)

[0095] - Component H [the bottom-type (39) compound which is an optical radical polymerization initiator] [0096]

[0097] [Table 2]

	硬化性(いぷね)	密着性	透明性	耐擦傷性	表面平 滑性
実施例1	7	0	0	0	0
実施例2	6	0	0	0	0
実施例3	3	0	0	0	0
実施例4	6	0	0	0	0
実施例 5	3	0	0	0	0
実施例 6	2	0	0	0	0
比較例1	3	Δ	Δ	Δ	Δ
比較例2	未硬化	_	_	_	_
比較例3	8	×	×	×	×

[0098] Except having used the polyethylene terephthalate film of 100-micrometer thickness, and the polyvinyl chloride film of 150-micrometer thickness using the constituent of example 7 examples 1-6, when the same actuation as an example 1 estimated, the good result as well as the case where a polycarbonate plate is used was obtained.

[0099]

[Effect of the Invention] A cure rate is quick, the paint film is excellent in adhesion, abrasion-proof nature, and surface smooth nature, and the activity energy-line hardening setup-of-tooling product for plastic linings of this invention has it as an object for the rebound ace courts of plastics. [especially useful]

[Translation done.]